



Comparison of oil and fuel particle chemical signatures with particle emissions from heavy and light duty vehicles

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Abstract

In order to establish effective vehicle emission control strategies, efforts are underway to perform studies which provide insight into the origin of the source of vehicle particle emissions. In this study, the mass spectral signatures of individual particles produced from atomized auto and diesel oil and fuel samples were obtained using aerosol time-of-flight mass spectrometry (ATOFMS). The major particle types produced by these samples show distinct chemistry, falling into several major categories for each sample. Lubricating oils contain calcium and phosphate based additives and although the additives are present in low abundance (~1–2% by mass), calcium and phosphate ions dominate the mass spectra for all new and used oil samples. Mass spectra from used oil contain more elemental carbon (EC) and organic carbon (OC) marker ions when compared to new oils and exhibit a very high degree of similarity to heavy duty diesel vehicle (HDDV) exhaust particles sampled by an ATOFMS. Fewer similarities exist between the used oil particles and light duty vehicle (LDV) emissions. Diesel and unleaded fuel mass spectra contain polycyclic aromatic hydrocarbon (PAH) molecular ions, as well as intense PAH fragment ions $^{25}(\text{C}_2\text{H})^-$, $^{49}(\text{C}_4\text{H})^-$, and inorganic ions $^{23}\text{Na}^+$, $^{39}\text{K}^+$, $^{95}(\text{PO}_4)^-$. Unleaded fuel produced spectra which contained Na^+ and K^+ ; likewise, LDV particle emission spectra also contained Na^+ and K^+ . Comparing oil and fuel particle signatures with HDDV and LDV emissions enhances our ability to differentiate between these sources and understand the origin of specific marker ions from these major ambient particle sources.

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1. Introduction

Atmospheric particles are chemically diverse, ranging from inorganic dust and soil to biological, organic, soot, and sea salt particles. Sources of the different particles in the atmosphere include wind

blown dust, vegetative pollen release, fuel combustion, secondary organic aerosol formation, and oceanic bubble bursting (Fitzgerald 1991; Graham et al., 2003; Pandis et al., 1992; Pinker et al., 2001). To understand the impact of particles on the environment, the ability to differentiate between particles from different sources and determine their ambient contributions is important. Fossil fuel combustion significantly contributes to the particle burden in urban areas (Hamilton and Mansfield,

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1991; Schauer and Cass, 2000) and these particles can be transported to non-urban areas as well (Hughes et al., 2000). Toxicologically, understanding the chemical composition of combustion particles is important because they have been linked to an increase in morbidity and adverse health effects (Collins et al., 1998; Dockery et al., 1992; Harrison and Yin, 2000; Schwartz et al., 1994; Weyand et al., 2004). Combustion particles have also been shown to affect climate by absorbing solar radiation and changing cloud properties (Ackerman et al., 2000; Andreae et al., 2004; Chung and Ramanathan, 2004; Chung et al., 2002; Krishnan and Ramanathan, 2002). Furthermore, atmospheric oxidation of unburned gasoline vapor has been shown to contribute to the formation of secondary organic aerosol (SOA) (Lee et al., 2004; Odum et al., 1997).

Light duty vehicles (LDV) and heavy duty diesel vehicles (HDDV) produce a significant number of particles composed of elemental carbon (EC), organic carbon (OC), trace metals, and salts (Burtcher et al., 1998; Kittelson, 1998; Kleeman et al., 2000; Lowenthal et al., 1994; Schauer et al., 1999, 2002; Silva and Prather, 1997; Suess and Prather, 2002). Oil and fuel formulations can influence the amount of the different species emitted from vehicles (Alander et al., 2004; Isotalo et al., 2002; Wang et al., 2000b), and these formulations vary by brand and type (Marr et al., 1999). Therefore, identical vehicles using fuel and oil produced by different vendors could potentially emit chemically distinct particles. Determining whether the majority of particulate matter produced by LDV and HDDV results from incomplete fuel combustion, unburned oil, or engine block elements will be useful for evaluating LDV and HDDV particulate emission control strategies, potentially leading to better fuel or oil formulations and/or engine design.

Aerosol time-of-flight mass spectrometry (ATOFMS) was used to analyze 16 different aerosolized fluids: new lubricating oil (10W-30), new lubricating oil (15W-40), used lubricating oil (10W-30), three used (15W-40) lubricating oils, four different 87 octane unleaded fuels, four different diesel fuels, and three diesel fuels taken from the fuel tank of different diesel trucks. The aim of this work is to study the variability of the mass spectral signatures from oil and fuel particles and compare them with LDV and HDDV emission particles. For LDV and HDDV sources, an understanding of the

origin of certain unique ions commonly observed in the single particle spectra will help unravel the differences observed for these two chemically similar ambient particle sources.

2. Methods

2.1. Single particle analysis: ATOFMS

Single particle chemical analysis was performed using a transportable dual ion ATOFMS instrument. A detailed instrumental description has been previously reported (Gard et al., 1997). Briefly, particles are drawn into the ATOFMS instrument through a converging nozzle inlet. Upon exiting the nozzle, the gas undergoes a supersonic expansion, causing particles to accelerate to different terminal velocities depending on their size and shape. Particles then pass through two 532 nm continuous wave (CW) lasers separated vertically by 60 mm. Scattered light caused by a particle passing through a CW laser is measured with a photomultiplier tube (PMT). The time difference between the two scattered light pulses is used to calculate particle velocity and ultimately aerodynamic size. The measured particle velocity is also used to time a Q-switched Nd:YAG laser to fire at the particle precisely as it enters the source region of a dual ion time-of-flight mass spectrometer. This Q-switched desorption/ionization laser was operated at 266 nm and ~ 1.0 mJ/pulse. ATOFMS measures the aerodynamic size and chemical composition of individual particles between 0.2 and 3.0 μm in real-time.

2.2. Fuel and oil particle generation

Unleaded and diesel fuel samples (numbered 1–4) were purchased from public gas stations in San Diego, California. New LDV and new HDDV oils were 10W-30 and 15W-40 blends, respectively. Unleaded (87 octane “regular”) auto fuel and diesel fuel samples (1–4) were stored in separate plastic petroleum storage containers for one week prior to experiment. Throughout this paper, the 87 octane auto fuel is referred to as “unleaded” and diesel fuel as “diesel”. HDDV fuel and HDDV used oil (numbered 1–3) were obtained from three separate diesel trucks (i.e. fuel tank or oil pan) that were used during an ATOFMS dynamometer study (Shields et al., 2006). Used LDV oil (10W-30) was obtained from a light duty pickup truck. All used oil samples

had a dark black visual appearance and were stored in glass containers. The number of operating hours on the engines for each used oil sample is unknown.

Fig. 1 shows a diagram of the particle generation setup. Particles from the fuels and oils were generated using a Collison nebulizer (May, 1973), followed by two Pyrex dilution chambers. Dry laboratory generated, charcoal, Purafil, and HEPA filtered air was used for aerosol production and subsequent dilution. A 2 L dilution chamber was utilized first, followed by a 1 L chamber. The dilution chambers each yielded about a 10-fold dilution for an overall dilution of the initial particle stream of 100-fold. Particle size distributions were measured using the ATOFMS instrument, an Aerodynamic Particle Sizer (APS, TSI Inc. model 3321), and a Scanning Mobility Particle Sizer (SMPS, TSI Inc. model 3936L10).

2.3. LDV and HDDV sampling

Methods for sampling LDV and HDDV emissions used for comparison in this study have been reported previously (Shields et al., 2006; Sodeman et al., 2005). Briefly, particle emissions from seven different HDDV were sampled on a HDDV transportable dynamometer (Bata et al., 1991). Twenty eight LDVs were run on a permanent dynamometer at the California Air Resources Board (CARB) vehicle testing facility in El Monte, CA. Vehicles were operated using a variety of standard testing cycles.

2.4. ATOFMS data analysis

Data were imported into Matlab Version 6.1.0.450 release 12.1 (The Math Works, Inc.) and analyzed

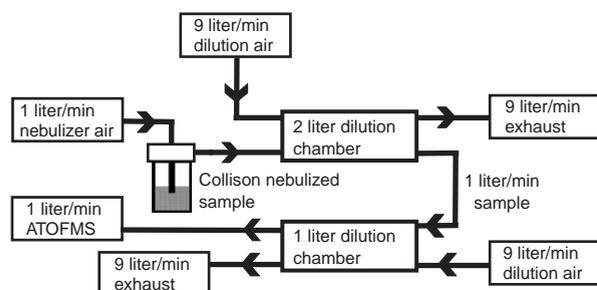


Fig. 1. Experimental setup. Oil and fuel particles are generated using a Collison nebulizer and diluted with dry, particle free air using a two stage dilution system prior to analysis with ATOFMS.

using YAADA version 1.2 [<http://www.yaada.org>]. Mathematical comparisons between the major LDV, HDDV and oil/fuel sample particle types were made using components of the YAADA toolkit.

were grouped using an Adaptive Resonance Theory neural network, ART-2a (Hopke and Song, 1997; Song et al., 2001, 1999). ART-2a groups particles together based on similarities between ion peak intensities in each individual particle mass spectrum. The parameters used for ART-2a in this experiment were: learning rate = 0.05, vigilance factor = 0.85, and iterations = 20. A particle cluster resulting from ART-2a can be used to generate a weight matrix (WM). The WM represents a weighted average of a group of similar mass spectra determined using ART-2a. The WM of different particle types can then be analyzed manually and further refined into distinct chemical classes. From this grouping of similar particles, an area matrix (AM) can then be generated. This AM represents the average intensity for each m/z for all particles within a group. In general, the AM strongly resembles the individual mass spectra of each particle within a group.

3. Results and discussion

For the following discussion, the presence and relative intensities of certain ion peaks are used to differentiate EC and OC (Spencer and Prather, 2006). EC is characterized by distinct carbon cluster ion peaks in the positive and negative mass spectra (12, 24, 36... C_n) that are typically higher in intensity than OC peaks occurring in the same spectra. OC peaks, such as m/z (15⁺, 27⁺, 29⁺, 37⁺, 43⁺, 25⁻, and 26⁻), can be assigned to a number of different organic fragments (McLafferty, 1980). Some of these include, ¹⁵(CH₃)⁺, ²⁷(C₂H₃)⁺, ²⁷(CNH)⁺, ²⁹(C₂H₅)⁺, ²⁹(COH)⁺, ⁴³(CHNO)⁺, ⁴³(C₂H₃O)⁺, ⁴³(C₃H₇)⁺, ⁹¹(C₇H₇)⁺, ²⁵(C₂H)⁻, and ²⁶(CN)⁻. Organic compounds can also produce ions at m/z 12, 24, 36, etc. (Silva and Prather, 2000), however, these are significantly lower in intensity than other OC markers at m/z 15⁺, 27⁺, 29⁺, 43⁺, 25⁻, and 26⁻.

Lab generated oil and diesel fuel particles ranged in size from 500 to 5000 nm (aerodynamic diameter). Oil particles from all samples produced a mode centered at roughly 2300 nm and the diesel fuel particle mode was centered at 1000 nm as measured by an APS. Very few oil and diesel fuel particles were generated within the size range

between 10 and 250 nm. Unleaded fuel particle sizes ranged from 20 to 250 and 500 to 1500 nm, as measured with an SMPS and APS, respectively. Unleaded fuel particles showed a mode at 100 nm on the SMPS and 670 nm on the APS. These size distributions are directly related to the method used to generate the particles, and a different formation method would produce different size distributions.

3.1. New and used oil samples

Fig. 2(a–d) contains the AM for the different particle classes detected in the new and used oil samples. Particle classes are labeled by order of ion intensity in the mass spectra. Fig. 2a shows the AM of a particle type containing Ca, phosphate, and OC that was observed exclusively in the new oils. Positive ion mass spectra of particles in this cluster

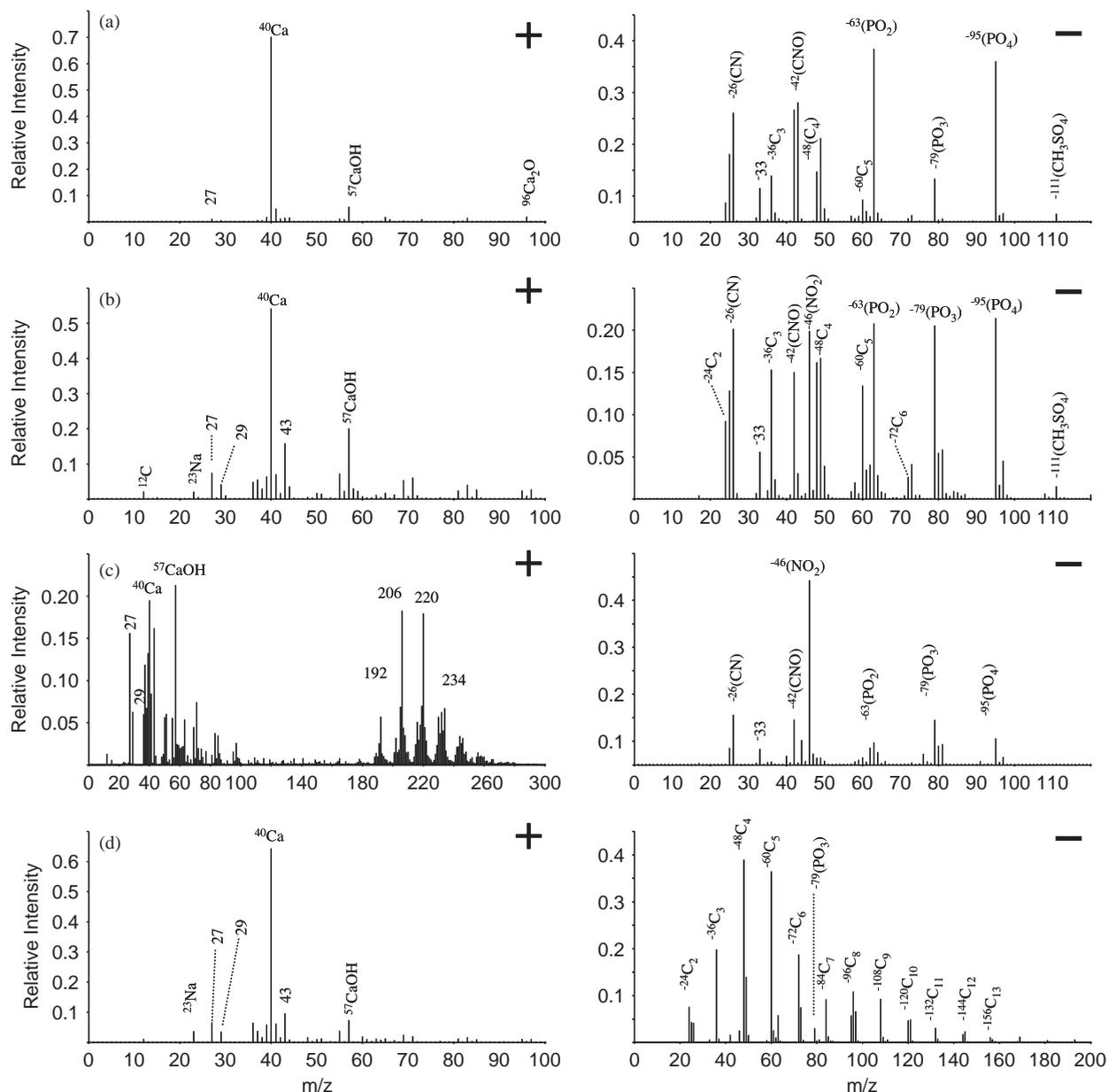


Fig. 2. Positive (left side) and negative (right side) ion AM for chemical classes detected in new and used oil samples. The five different major classes shown are: (a) Ca–phosphate–OC; (b) Ca–EC–OC–phosphate–NO₂–Na; (c) Ca–PAH–OC–phosphate; and (d) Ca–EC–OC–phosphate. Mass-to-charge values and chemical assignment for some ions are given above the peak.

are dominated by an intense $^{40}\text{Ca}^+$ peak as well as peaks at $^{57}(\text{CaOH})^+$, $^{96}(\text{Ca}_2\text{O})^+$, and $m/z\ 27^+$. The peak at 27^+ is most likely $^{27}\text{HCN}^+$, based on the simultaneous presence of an intense $^{26}(\text{CN})^-$ in the negative ion spectra of the same particle, and attributed to the presence of nitrogen-containing organics (Silva and Prather, 2000). The corresponding negative ion spectrum in Fig. 2a shows the presence of phosphate $^{63}(\text{PO}_2)^-$, $^{79}(\text{PO}_3)^-$, and $^{95}(\text{PO}_4)^-$ / $^{95}(\text{CH}_3\text{SO}_3)^-$, carbon clusters out to $^{60}\text{C}_5^-$, $^{26}(\text{CN})^-$, $^{42}(\text{CNO})^-$, and $^{111}(\text{CH}_3\text{SO}_4)^-$. Calcium is added to engine lubricants as part of a detergent complex as well as to serve as a base to neutralize acids and stabilize highly polar compounds that are formed in the engine during combustion (Lyyranen et al., 1999; Rudnick, 2003). Zinc dialkyldithiophosphate (ZDDP) is also added to commercial lubricants and serves as an anti-wear and extreme-pressure agent (Gautam et al., 1999). ZDDP and the thermo-oxidative breakdown products orthophosphate and pyrophosphate have been measured in lubricant films, and therefore the presence of phosphates is expected (Canning et al., 1999; Willermet et al., 1992). The presence of zinc is also expected, however due to a relatively low sensitivity of the ATOFMS instrument to organometallic zinc, no zinc ions were detected during this study. It is important to note that calcium makes up 1–2% of the oil mass, however the calcium ion peak at $m/z\ 40^+$ dominates the spectrum, demonstrating how Ca^+ can suppress the organic and trace metal ion intensities in this matrix. Furthermore, desorption and ionization of base mineral oil which did not contain the additive package (i.e. no calcium and phosphate) at the same wavelength (266 nm laser) and power (1.5 mJ) produced only a few particle spectra containing low intensity ions, indicating weak absorption. This is not surprising given the composition of mineral oil is dominated by long chain hydrocarbons which do not absorb 266 nm radiation. However, the oil samples in these experiments which did include additive packages strongly absorbed the 266 nm radiation.

Figs. 2b–d show the AM for particles detected in used LDV and HDDV oil samples. Fig. 2b shows the particle type (Ca–EC–OC–phosphate– NO_2 –Na) that is readily distinguished from the new oil shown in Fig. 2a by the increased intensities of the EC ion peaks ($^{36}\text{C}_3^-$, $^{48}\text{C}_4^-$, $^{60}\text{C}_5^-$, $^{72}\text{C}_7^-$), OC ion markers (i.e. 27^+ , 29^+ , 43^+ , 55^+ , 69^+ , 71^+ , 81^+ , 83^+ , 85^+ , 93^+ , 95^+), the presence of $^{23}\text{Na}^+$, and an intense

peak at $^{46}(\text{NO}_2)^-$. Normal and branched alkanes typically fragment to ions at $m/z\ 29^+$, 43^+ , 57^+ , and 71^+ , while alkenes and cycloalkanes will yield ions at $m/z\ 27^+$, 41^+ , 55^+ , 69^+ and 83^+ (McLafferty, 1980). These fragment ions are observed for used oil and HDDV exhaust particles by the ATOFMS instrument, as well as in previous studies with a thermal desorption particle beam mass spectrometer and an Aerodyne aerosol mass spectrometer (AMS) (Alfarra et al., 2004; Canagaratna et al., 2004; Tobias et al., 2001). These are most likely the non-absorbing aliphatic hydrocarbons in the base oil described above. Apparently, the additional EC in these particles acts as a strongly absorbing matrix, enhancing the signals from these non-absorbing aliphatic species in direct analogy to matrix assisted laser desorption ionization (Karas and Kruger, 2003). The presence of a strong peak at $m/z\ 46$ can be explained by several factors. NO_x formation occurs during the combustion process from reactions between oxygen and nitrogen in the fuel-air mixture (Heywood, 1988). It can react to form nitrogen-containing species that can then be absorbed into the oil and stabilized as inorganic salts (Rudnick, 2003). It has also been shown that nitro-PAH's commonly fragment into CN^- and NO_2^- when ionized using a 266 nm laser which was used in these experiments (Bezabeh et al., 1997). Peaks at $^{26}(\text{CN})^-$ and $^{46}(\text{NO}_2)^-$ could therefore derive from nitro-PAH's which have been measured in both used oil and diesel exhaust particles (Bezabeh et al., 1997; Zielinska et al., 2004).

Used LDV oil particles are distinguished from HDDV oil particles by the unique particle class (Ca–PAH–OC–phosphate) shown in Fig. 2c. This particle type is characterized by a $^{40}\text{Ca}^+$ peak, OC peaks at 27^+ , 29^+ , and intense ion signals at 192^+ , 206^+ , 220^+ and 234^+ . Each of these ions are separated by a mass difference of 14, which suggests they could be phenanthrene, anthracene, or possibly heteroatom PAH's with increasing numbers of methyl or ethyl substituents. Previous work has shown that over one hundred different PAH species accumulate in LDV oil over prolonged vehicle operation (Wang et al., 2000a). Zielinska (2004) and Wong (2001) observed similar PAH species in oil, fuel, and HDDV and LDV tailpipe emissions. Zielinska (2004) also shows that lubricating oil in gasoline engines contains a larger amount of PAH's compared to diesel oil.

All three used HDDV oils contained a significant amount of the Ca–EC–OC–phosphate particle type.

In Fig. 2d, the positive ion AM for this particle class shows dominant peaks for $^{40}\text{Ca}^+$, $^{57}(\text{CaOH})^+$, $^{96}(\text{Ca}_2\text{O})^+$, and OC peaks 27^+ , 29^+ and 43^+ . The negative ion AM shows a carbon envelope extending out to $^{156}\text{C}_{13}^-$ and the presence of $^{63}(\text{PO}_2)^-$, $^{79}(\text{PO}_3)^-$, and $^{95}(\text{PO}_4)^-$. It has been well documented that diesel powered engines generate more EC than spark ignition engines (Burtcher et al., 1998; Zielinska et al., 2004). One function of lubricating oil is to help disperse agglomerated EC particles in the oil. Because diesel engines generate more EC, more EC agglomerates are observed in the used HDDV oil than the used LDV oil.

3.2. Diesel fuel samples

Diesel fuel and regular unleaded fuel particles are readily distinguished from each other based on the presence of unique PAH ions. Fig. 3 shows the AM that makes up between 40 and 80% of the mass spectra for the different diesel fuel samples. This class is labeled *PAH-containing* and is comprised of any clusters containing intense ion signals at m/z 181^+ , 195^+ , 206^+ , 220^+ , 234^+ and m/z 193^- , 207^- , 208^- , 222^- , and 236^- . Two series of PAH are observed, one at m/z 181^+ and 195^+ (separated by 14 amu) and the other series at m/z 206^+ , 220^+ , 234^+ (also separated by 14 amu). PAH compounds have been shown to comprise a large fraction of diesel fuel (Rhead and Hardy, 2003). The formation of negative ion PAH species is a unique feature of the diesel fuel. One possible explanation for the negative ion PAHs is they contain electronegative functionalities such as oxy-PAHs which have been measured in diesel fuel (Zielinska et al., 2004). For example, anthraquinone, has a molecular weight (MW) of 208, and methyl-anthraquinone has a MW of 222. However, assignment of these negative ions to oxy-PAHs is speculative until further analysis is

performed on these samples. Peaks for OC are also observed at m/z , 27^+ , 29^+ , 43^+ , $^{26}(\text{CN})^-$, 25^- , and 49^- . Ions at 25^- , 49^- , and 73^- have been shown to come from PAH fragmentation (Silva and Prather, 2000).

3.3. Unleaded fuel samples

Fig. 4(a–e) shows the AM for the five different particle classes that are unique to the unleaded fuel samples. Each of the particle classes shown in Fig. 4 contain PAH fragment ions at 25^- , 49^- , 73^- and sulfate peaks at $^{97}(\text{HSO}_4)^-$. Organic carbon fragment peaks at m/z $^{15}\text{CH}_3^+$, 27^+ , 29^+ , 43^+ , sulfur-containing ions at $^{80}(\text{SO}_3)^-$ and $^{81}(\text{HSO}_3)^-$ and peaks at m/z 109^- , 123^- , and 137^- are also observed in many of the AM shown in Fig. 4.

Shown in Fig. 4a is the AM of particles observed for all of the unleaded fuel samples (PAH–sulfate– NO_2 –Cl). The AM of this particle type is characterized by intense peaks attributed to PAH ions at m/z , 192^+ , 206^+ , 218^+ , 230^+ , and 242^+ , as well as peaks due to $^{35}\text{Cl}^-$ and $^{46}(\text{NO}_2)^-$. The largest fraction of particles in the unleaded fuel samples were an OC–K–Na–sulfate–phosphate type, shown in Fig. 4b. The presence of potassium in this unleaded fuel class distinguishes it from diesel fuel. Potassium is not generally used as a fuel additive; however it is clearly present in all of the unleaded fuel samples. ATOFMS has a high sensitivity to potassium so even though it is present in low concentrations in fuel, it produces a large ion peak in the ATOFMS spectra (Gross et al., 2000). Phosphate $^{79}(\text{PO}_3)^-$ and carbon cluster peaks extending out to m/z 72^- also are detected in Fig. 4b negative ion AM. Unleaded fuel samples #1 and #3 contain an OC–sulfate–phosphate particle class which is unique to these samples (Fig. 4c). This AM contains unique peaks at 130^+ , 162^+ , and

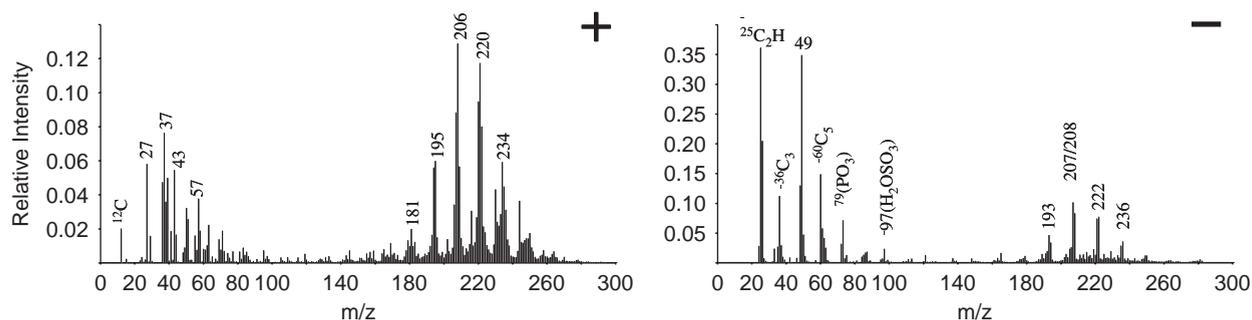


Fig. 3. Positive and negative ion AM for PAH-containing particle class detected exclusively in diesel fuel.

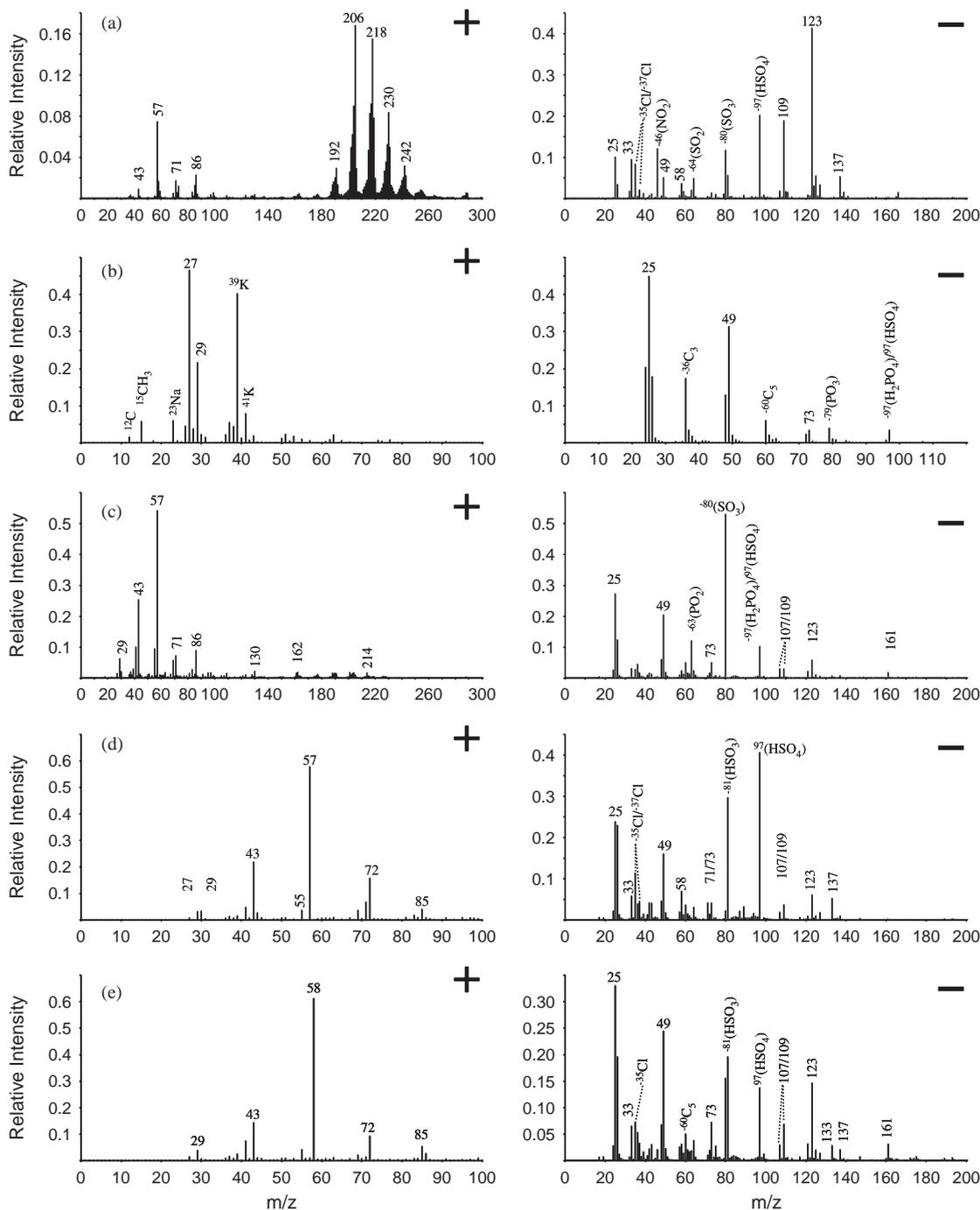


Fig. 4. Positive and negative ion AM for five particle types unique to unleaded fuel. The five different types shown are: (a) PAH-sulfate-NO₂-Cl; (b) OC-K-Na-sulfate-phosphate; (c) OC-sulfate-phosphate; (d) OC-sulfur containing; and (e) OC-sulfate-other.

214⁺, that other fuel types did not contain. Figs. 4d and 4e show the AMs for OC particle classes almost exclusive to unleaded fuel samples #2 and #4, respectively. The major difference between Figs. 4d

and e is an ion at m/z 57⁺ (Fig. 4d), instead of 58⁺ (Fig. 4e).

Both unleaded and diesel fuel produced an OC-Na-sulfate-phosphate particle class. Fig. 5

shows the AM for this class characterized by the presence of OC at 27^+ , 29^+ , 43^+ , 91^+ , PAH fragment ions at 25^- , 49^- , 73^- , sulfate at $^{97}(\text{HSO}_4)^-$, and phosphate at $^{79}(\text{PO}_3)^-$. Higher molecular weight ions at 165^+ , 179^+ , and 193^+ are present as well. These ions could be attributed to nitrogen-containing aromatics with alkyl substitutions based on the presence of odd masses (McLafferty, 1980). Further, ions at m/z 119^+ , 105^+ , 91^+ are attributed to fragmentation of phenylalkyl (substituted mono-aromatic) type com-

pounds (McLafferty, 1980). However, given the enormous number of organic species present in gasoline and diesel fuels, these assignments are somewhat speculative without further analysis.

Fig. 6 shows the fractional contributions of the different particles types for each oil and fuel sample determined using ART-2a analysis. Fig. 6 clearly shows that new oil, used oil, diesel fuel, and unleaded fuel can be distinguished from each other at the single particle level. New oil samples are dominated by calcium, phosphate, and OC

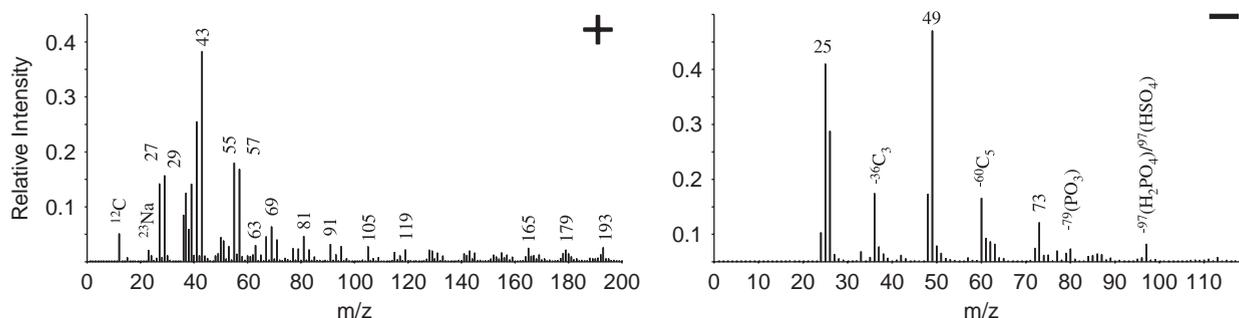


Fig. 5. Positive and negative ion AM for the OC–Na–sulfate–phosphate particle class detected in both diesel and unleaded fuel samples.

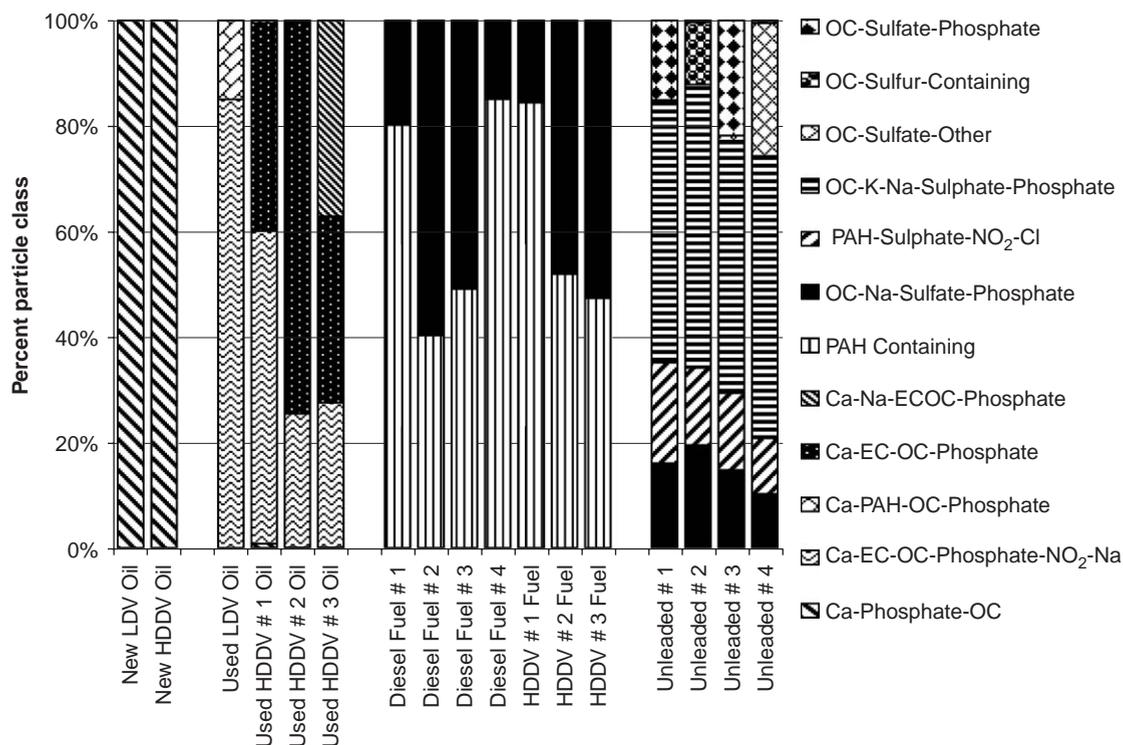


Fig. 6. Histogram showing the percent contribution of each particle class to each oil and fuel sample analyzed. Oil or fuel type is listed across the x-axis, and the percent (normalized) of each particle class observed within a sample is given on the y-axis. Colors corresponding to different particle classes are listed in the legend.

signatures (Ca–phosphate–OC chemical class). Used HDDV oil samples show additional marker ions from NO_2^- and Na^+ (Ca–EC–OC–phosphate– NO_2^- –Na), as well as EC (Ca–ECOC–phosphate). Used LDV oil differs from used HDDV oil by the presence of PAH-containing particles (Ca–PAH–OC–phosphate type). Diesel fuel particle mass spectra are dominated by PAH's (40–80% of particles contain PAHs), OC, Na, sulfates, and phosphates. The majority (50%) of unleaded fuel particles contained K^+ , which differentiates it from diesel fuel. Furthermore, a fraction (10–20%) of unleaded fuel particles contained PAH, NO_2 , and Cl ions, another distinguishing feature.

3.4. Comparison with PM emissions

When comparing particle types observed in fuel and oil samples with HDDV exhaust particles

between 500 and 2500 nm, the calcium and phosphate dominated types (Ca–OC–phosphate– NO_2^- –Na and Ca–ECOC–phosphate) detected in the used HDDV oil samples show a strong degree of similarity to the most dominant particle type detected in HDDV exhaust. The dot products of the weight matrices for the used oil particle types (Ca–EC–OC–phosphate– NO_2^- –Na and Ca–ECOC–phosphate particle class) with the corresponding HDDV exhaust particle types were 0.87 and 0.85, respectively. A significant fraction (~60%) of freshly emitted HDDV particles in the 500–2500 nm size range showed the same mass spectral fingerprint as used HDDV oil (Shields et al., 2006). Figs. 7a and 7b show the dual ion AM for the Ca–ECOC–phosphate mass spectral class from used oil and the AM for the most abundant particle class from a HDDV dynamometer study using ATOFMS (Shields et al., 2006). By visual

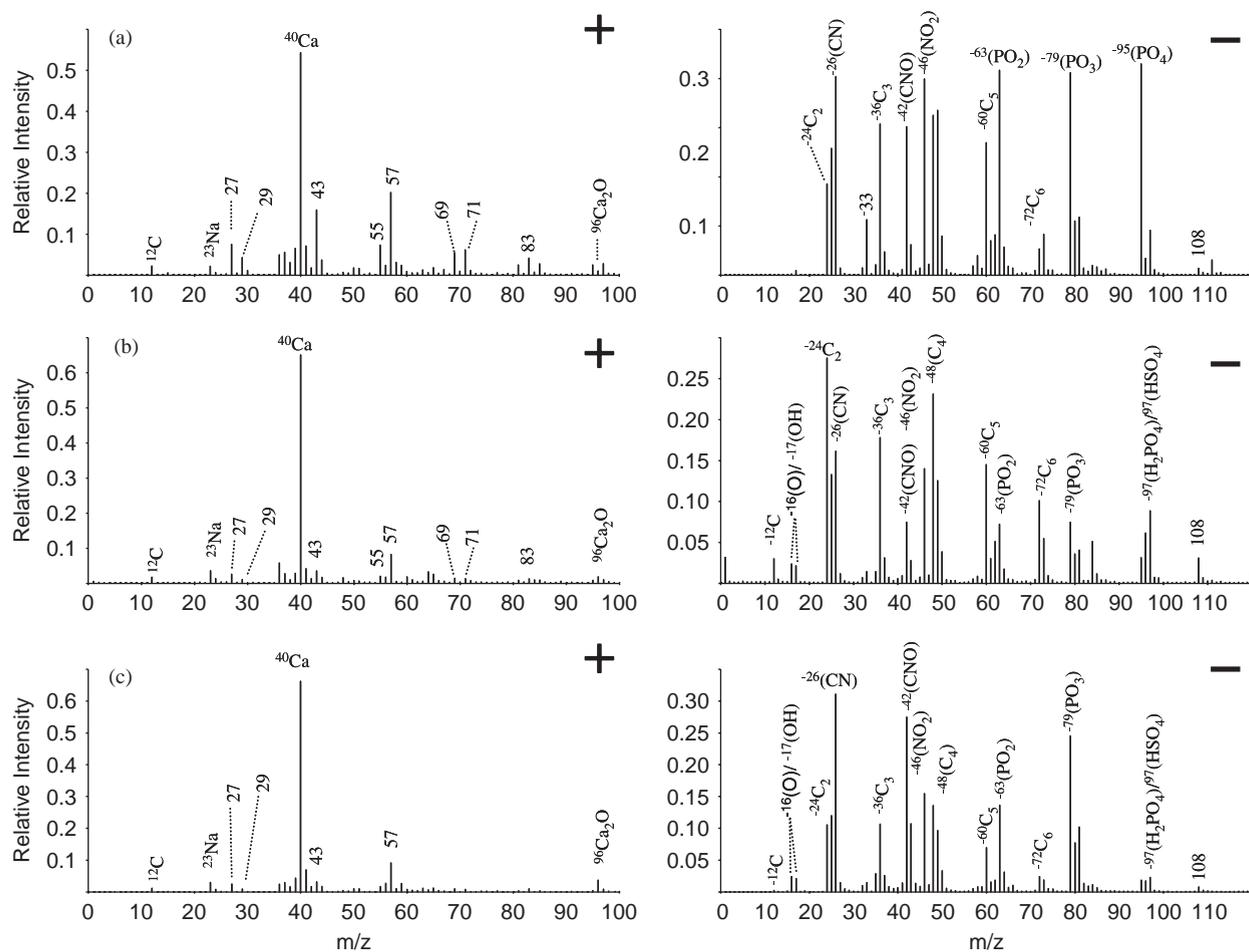


Fig. 7. Comparison of (a) the Ca–ECOC–phosphate AM from used oil; (b) the AM of the largest particle class from the exhaust of heavy duty diesel trucks; and (c) the AM of a class of particles that made up ~2% of “smoker” LDV mass spectra.

inspection, one can see the two area matrices are strikingly similar. Shields (2006) and Toner (2006) show that a dominant particle class from diesel trucks from 50–500 nm is an EC–Ca particle type which differs from the Ca–ECOC–phosphate type discussed above in the relative intensity of the Ca^+ ion peak to the carbon ion clusters in the positive ion mass spectra. This would suggest that EC particles in this smaller size range from diesel trucks are a mixture of freshly generated EC with a small fraction of unburned oil. These findings are consistent with a previous report that states up to 95% of the volatile component of nanoparticles and accumulation-mode particles emitted from diesel trucks are from unburned oil (Sakurai et al., 2003). Other research has shown a significant fraction of Ca coming from fuel (Sharma et al., 2005; Wang et al., 2003). Data here would suggest that unburned oil might also be a significant source of Ca in diesel particle emissions.

Recent results from a study by Shields (2006) show that the particle emissions can reflect the oil signatures from HDDV trucks. Specifically, a particle type from used oil showed increased amounts of Na (HDDV #3 oil); correspondingly, the emissions from the HDDV from which this sample was taken produced exhaust particle spectra with higher amounts of Na^+ . This finding provides further evidence that HDDV exhaust particles contain a significant fraction of unburned oil and that the chemical composition of the oil is reflected in the chemistry of the HDDV particle emissions.

Comparison of the dominant particle class detected in used LDV oil with LDV exhaust particle classes yielded few similarities, suggesting that LDV emissions are not normally composed of a large fraction of unburned oil. However, one LDV that emitted heavy amounts of smoke from its tailpipe (i.e. “smoker”) did contain a small fraction (~2%) of the LDV oil particle class (Ca–OC–phosphate– NO_2 –Na). The area matrix for the comparable particle class from the LDV smoker is shown in Fig. 7c for comparison with the HDDV oil type (Sodeman et al., 2005).

Unleaded fuel and diesel fuel particles do not resemble LDV and HDDV exhaust particles, suggesting vehicle emissions do not contain a large fraction of unburned fuel particles. However unburned fuel vapor could condense on other particle cores; these vapor coated particles may not be comparable to pure fuel particles. Potassium and sodium were observed in the fuel samples and

LDV emissions also show peaks due to K^+ and Na^+ (Shields et al., 2006; Sodeman et al., 2005; Toner et al., 2006), suggesting that these elements could be coming from the fuel.

4. Conclusions

To differentiate between fresh particle emissions from HDDV and LDV (with the exception of “smoker” LDV) using ATOFMS, the used HDDV oil particle mass spectra provide good indicators for HDDV exhaust particles. Using ATOFMS, lubricating oil is characterized by a very intense Ca^+ peak accompanied by less intense organic fragment ions. Ambient particles sampled using ATOFMS containing a combination of intense Ca^+ , CaOH^+ , and EC/OC marker ions are likely to be fresh diesel combustion particles composed of a significant amount of unburned lubricating oil. Comparing oil and fuel particle signatures with particle characterization studies of HDDV and LDV emissions enhances our ability to differentiate between HDDV and LDV sources and understand the origin of specific marker ions from these major ambient particle sources.

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References

- Ackerman, A.S., Toon, O.B., Stevens, D.E., Heymsfield, A.J., Ramanathan, V., Welton, E.J., 2000. Reduction of tropical cloudiness by soot. *Science* 288, 1042–1047.
- Alander, T.J.A., Leskinen, A.P., Raunemaa, T.M., Rantanen, L., 2004. Characterization of diesel particles: effects of fuel reformulation, exhaust after treatment, and engine operation on particle carbon composition and volatility. *Environmental Science & Technology* 38, 2707–2714.
- Alfarra, M.R., Coe, H., Allan, J.D., Bower, K.N., Boudries, H., Canagaratna, M.R., Jimenez, J.L., Jayne, J.T., Garforth, A.A., Li, S.M., Worsnop, D.R., 2004. Characterization of urban and rural organic particulate in the Lower Fraser Valley using two aerodyne aerosol mass spectrometers. *Atmospheric Environment* 38, 5745–5758.
- Andreae, M.O., Rosenfeld, D., Artaxo, P., Costa, A.A., Frank, G.P., Longo, K.M., Silva-Dias, M.A.F., 2004. Smoking rain clouds over the Amazon. *Science* 303, 1337–1342.
- Bata, R., Clark, N., Gautam, M., Howell, A., Long, T., Loth, J., Lyons, D., Palmer, G., Smith, J., Wang, W., 1991. A transportable heavy duty engine testing laboratory. *SAE Transactions* 100, 433–440.

- Bezabeh, D.Z., Allen, T.M., McCauley, E.M., Kelly, P.B., Jones, A.D., 1997. Negative ion laser desorption ionization time-of-flight mass spectrometry of nitrated polycyclic aromatic hydrocarbons. *Journal of the American Society for Mass Spectrometry* 8, 630–636.
- Burtscher, H., Kunzel, S., Hüglin, C., 1998. Characterization of particles in combustion engine exhaust. *Journal of Aerosol Science* 29, 389–396.
- Canagaratna, M.R., Jayne, J.T., Ghertner, D.A., Herndon, S., Shi, Q., Jimenez, J.L., Silva, P.J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K.L., Kolb, C.E., Worsnop, D.R., 2004. Chase studies of particulate emissions from in-use New York city vehicles. *Aerosol Science and Technology* 38, 555–573.
- Canning, G.W., Fuller, M.L.S., Bancroft, G.M., Kasrai, M., Cutler, J.N., De Stasio, G., Gilbert, B., 1999. Spectro-microscopy of tribological films from engine oil additives. Part I. Films from ZDDP's. *Tribology Letters* 6, 159–169.
- Chung, C.E., Ramanathan, V., 2004. Aerosol loading over the Indian Ocean and its possible impact on regional climate. *Indian Journal of Marine Sciences* 33, 40–55.
- Chung, C.E., Ramanathan, V., Kiehl, J.T., 2002. Effects of the South Asian absorbing haze on the northeast monsoon and surface—air heat exchange. *Journal of Climate* 15, 2462–2476.
- Collins, J.F., Brown, J.P., Alexeeff, G.V., Salmon, A.G., 1998. Potency equivalency factors for some polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbon derivatives. *Regulatory Toxicology and Pharmacology* 28, 45–54.
- Dockery, D.W., Schwartz, J., Spengler, J.D., 1992. Air pollution and daily mortality: associations with particulates and acid aerosols. *Environmental Research* 59, 362–373.
- Fitzgerald, J.W., 1991. Marine aerosols—a review. *Atmospheric Environment Part A—General Topics* 25, 533–545.
- Gard, E., Mayer, J.E., Morrical, B.D., Dienes, T., Ferguson, D.P., Prather, K.A., 1997. Real-time analysis of individual atmospheric aerosol particles: design and performance of a portable ATOFMS. *Analytical Chemistry* 69, 4083–4091.
- Gautam, M., Chitoor, K., Durbha, M., Summers, J.C., 1999. Effect of diesel soot contaminated oil on engine wear—investigation of novel oil formulations. *Tribology International* 32, 687–699.
- Graham, B., Guyon, P., Taylor, P.E., Artaxo, P., Maenhaut, W., Glovsky, M.M., Flagan, R.C., Andreae, M.O., 2003. Organic compounds present in the natural Amazonian aerosol: characterization by gas chromatography—mass spectrometry. *Journal of Geophysical Research-Atmospheres* 108(D24), 4766.
- Gross, D.S., Galli, M.E., Silva, P.J., Prather, K.A., 2000. Relative sensitivity factors for alkali metal and ammonium cations in single particle aerosol time-of-flight mass spectra. *Analytical Chemistry* 72, 416–422.
- Hamilton, R.S., Mansfield, T.A., 1991. Airborne particulate elemental carbon—its sources, transport and contribution to dark smoke and soiling. *Atmospheric Environment Part A—General Topics* 25, 715–723.
- Harrison, R.M., Yin, J.X., 2000. Particulate matter in the atmosphere: which particle properties are important for its effects on health? *Science of the Total Environment* 249, 85–101.
- Heywood, J.B., 1988. *Internal Combustion Engine Fundamentals*. McGraw-Hill, New York vol. xxix, pp. 930–932.
- Hopke, P.K., Song, X.H., 1997. Classification of single particles by neural networks based on the computer-controlled scanning electron microscopy data. *Analytica Chimica Acta* 348, 375–388.
- Hughes, L.S., Allen, J.O., Bhave, P., Kleeman, M.J., Cass, G.R., Liu, D.Y., Ferguson, D.F., Morrical, B.D., Prather, K.A., 2000. Evolution of atmospheric particles along trajectories crossing the Los Angeles basin. *Environmental Science & Technology* 34, 3058–3068.
- Isotalo, S., Kuljukka-Rabb, T., Rantanen, L., Mikkonen, S., Savela, K., 2002. The effect of diesel fuel reformulation on the exhaust measured by Ames mutagenicity and DNA adducts. *International Journal of Environmental Analytical Chemistry* 82, 87–95.
- Karas, M., Kruger, R., 2003. Ion formation in MALDI: the cluster ionization mechanism. *Chemical Reviews* 103, 427–439.
- Kittelson, D.B., 1998. Engines and nanoparticles: a review. *Journal of Aerosol Science* 29, 575–588.
- Kleeman, M.J., Schauer, J.J., Cass, G.R., 2000. Size and composition distribution of fine particulate matter emitted from motor vehicles. *Environmental Science & Technology* 34, 1132–1142.
- Krishnan, R., Ramanathan, V., 2002. Evidence of surface cooling from absorbing aerosols. *Geophysical Research Letters* 29.
- Lee, S.D., Jang, M.S., Kamens, R.M., 2004. Soa formation from the photooxidation of alpha-pinene in the presence of freshly emitted diesel soot exhaust. *Atmospheric Environment* 38, 2597–2605.
- Lowenthal, D.H., Zielinska, B., Chow, J.C., Watson, J.G., Gautam, M., Ferguson, D.H., Neuroth, G.R., Stevens, K.D., 1994. Characterization of heavy-duty diesel vehicle emissions. *Atmospheric Environment* 28, 731–743.
- Lyyranen, J., Jokiniemi, J., Kauppinen, E.I., Joutsensaari, J., 1999. Aerosol characterisation in medium-speed diesel engines operating with heavy fuel oils. *Journal of Aerosol Science* 30, 771–784.
- Marr, L.C., Kirchstetter, T.W., Harley, R.A., Miguel, A.H., Hering, S.V., Hammond, S.K., 1999. Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. *Environmental Science & Technology* 33, 3091–3099.
- May, K.R., 1973. Collision nebulizer. Description, performance, and application. *Journal of Aerosol Science* 4, 235–243.
- McLafferty, F.W., 1980. *Interpretation of Mass Spectra*, third ed. p. 303.
- Odum, J.R., Jungkamp, T.P.W., Griffin, R.J., Flagan, R.C., Seinfeld, J.H., 1997. The atmospheric aerosol-forming potential of whole gasoline vapor. *Science* 276, 96–99.
- Pandis, S.N., Harley, R.A., Cass, G.R., Seinfeld, J.H., 1992. Secondary organic aerosol formation and transport. *Atmospheric Environment Part A—General Topics* 26, 2269–2282.
- Pinker, R.T., Pandithurai, G., Holben, B.N., Dubovik, O., Aro, T.O., 2001. A dust outbreak episode in Sub-Sahel West Africa. *Journal of Geophysical Research-Atmospheres* 106, 22923–22930.
- Rhead, M.M., Hardy, S.A., 2003. The sources of polycyclic aromatic compounds in diesel engine emissions. *Fuel* 82, 385–393.
- Rudnick, L.R., 2003. *Lubricant Additives: Chemistry and Applications*. M. Dekker, New York vol. xiii, p. 735.

- Sakurai, H., Tobias, H.J., Park, K., Zarling, D., Docherty, S., Kittelson, D.B., McMurry, P.H., Ziemann, P.J., 2003. On-line measurements of diesel nanoparticle composition and volatility. *Atmospheric Environment* 37, 1199–1210.
- Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environmental Science & Technology* 34, 1821–1832.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks. *Environmental Science & Technology* 33, 1578–1587.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles. *Environmental Science & Technology* 36, 1169–1180.
- Schwartz, J., Dockery, D.W., Neas, L.M., Wypij, D., Ware, J.H., Spengler, J.D., Koutrakis, P., Speizer, F.E., Ferris, B.G., 1994. Acute effects of summer air-pollution on respiratory symptom reporting in children. *American Journal of Respiratory and Critical Care Medicine* 150, 1234–1242.
- Sharma, M., Agarwal, A.K., Bharathi, K.V.L., 2005. Characterization of exhaust particulates from diesel engine. *Atmospheric Environment* 39, 3023–3028.
- Shields, L.G., Suess, D.T., Prather, K.A., 2006. Determination of single particle mass spectral signatures from heavy duty vehicle emissions for PM_{2.5} source apportionment. *Atmospheric Environment*, submitted.
- Silva, P.J., Prather, K.A., 1997. On-line characterization of individual particles from automobile emissions. *Environmental Science & Technology* 31, 3074–3080.
- Silva, P.J., Prather, K.A., 2000. Interpretation of mass spectra from organic compounds in aerosol time-of-flight mass spectrometry. *Analytical Chemistry* 72, 3553–3562.
- Sodeman, D.A., Toner, S.M., Prather, K.A., 2005. Determination of single particle mass spectral signatures from light-duty vehicle emissions. *Environmental Science and Technology* 39, 4569–4580.
- Song, X.H., Hopke, P.K., Fergenson, D.P., Prather, K.A., 1999. Classification of single particles analyzed by ATOFMS using an Artificial Neural Network, Art-2a. *Analytical Chemistry* 71, 860–865.
- Song, X.H., Faber, N.M., Hopke, P.K., Suess, D.T., Prather, K.A., Schauer, J.J., Cass, G.R., 2001. Source apportionment of gasoline and diesel by multivariate calibration based on single particle mass spectral data. *Analytica Chimica Acta* 446, 329–343.
- Spencer, M.T., Prather, K.A., 2006. Using ATOFMS to estimate the fractions of Ec and Oc in particles. *Aerosol Science and Technology* 40, 585–594.
- Suess, D.T., Prather, K.A., 2002. Reproducibility of single particle chemical composition during a heavy duty diesel truck dynamometer study. *Aerosol Science and Technology* 36, 1139–1141.
- Tobias, H.J., Beving, D.E., Ziemann, P.J., Sakurai, H., Zuk, M., McMurry, P.H., Zarling, D., Waytulonis, R., Kittelson, D.B., 2001. Chemical analysis of diesel engine nanoparticles using a nano-DMA/thermal desorption particle beam mass spectrometer. *Environmental Science & Technology* 35, 2233–2243.
- Toner, S.M., Sodeman, D.A., Prather, K.A., 2006. Single particle characterization of ultrafine and accumulation mode particles from heavy duty diesel vehicles using aerosol time-of-flight mass spectrometry. *Environmental Science & Technology*, ASAP article.
- Wang, J., Jia, C.R., Wong, C.K., Wong, P.K., 2000a. Characterization of polycyclic aromatic hydrocarbons created in lubricating oils. *Water Air and Soil Pollution* 120, 381–396.
- Wang, W.G., Lyons, D.W., Clark, N.N., Gautam, M., Norton, P.M., 2000b. Emissions from nine heavy trucks fueled by diesel and biodiesel blend without engine modification. *Environmental Science & Technology* 34, 933–939.
- Wang, Y.F., Huang, K.L., Li, C.T., Mi, H.H., Luo, J.H., Tsai, P.J., 2003. Emissions of fuel metals content from a diesel vehicle engine. *Atmospheric Environment* 37, 4637–4643.
- Weyand, E.H., Parimoo, B., Reuhl, K.R., Goldstein, L.S., Wang, J.Q., Harvey, R.G., 2004. 7H-Benzo [C] fluorene: a potent systemic lung carcinogen. *Polycyclic Aromatic Compounds* 24, 1–20.
- Willermet, P.A., Carter, R.O., Boulos, E.N., 1992. Lubricant-derived tribochemical films—an infrared spectroscopic study. *Tribology International* 25, 371–380.
- Wong, P.K., Wang, J., 2001. The accumulation of polycyclic aromatic hydrocarbons in lubricating oil over time – a comparison of supercritical fluid and liquid-liquid extraction methods. *Environmental Pollution* 112, 407–415.
- Zielinska, B., Sagebiel, J., McDonald, J.D., Whitney, K., Lawson, D.R., 2004. Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *Journal of the Air & Waste Management Association* 54, 1138–1150.